CONTRIBUTION FROM E. I. DU PONT DE NEMOURS AND CO., INC., EXPLOSIVES DEPARTMENT,
EXPERIMENTAL STATION LABORATORY, WILMINGTON, DELAWARE 19898

Phosphorus–Fluorine Chemistry. XIX.[1] The Reaction of Cyclic Aminosilanes with Fluorophosphoranes

BY R. SCHMUTZLER[2]

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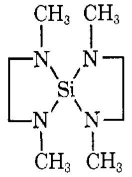
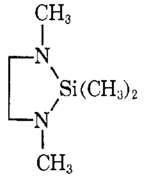
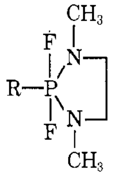
Tetrafluorophosphoranes were found to react with certain cyclic aminosilanes with formation of products involving phosphorus as part of a five-membered C–N–P–N–C ring system. The identity of these products as phosphonium pentafluorophosphates has been established from their H^1, F^{19}, and P^{31} nmr spectra.

Introduction

In a number of recent publications it has been demonstrated that the cleavage reaction of silicon–nitrogen bonds by fluorophosphoranes provides a versatile method of synthesis for various novel phosphorus–nitrogen compounds.[3,4] Numerous new silicon–nitrogen systems have become available recently, and an extension of the earlier work[3,4] as to involve such compounds was indicated. The present work, in particular, deals with the reaction of some tetrafluorophosphoranes with two cyclic aminosilanes: N,N,N′,N′-tetramethylspiro[silaimidazolidine] (I)[5] and 1,2,2,3-tetramethyl-1,3-diaza-2-silacyclopentane (II).[6] The expectation was that it might be possible to attach the N–C–C–N grouping onto the pentacoordinate phosphorus atom of the fluorophosphorane with formation of a cyclic compound of the type


I


II


III

The fact that phosphorus would be part of a small ring system might impose certain special features on the stereochemistry of compounds of type III which might be reflected in their F^{19} and P^{31} nmr spectra.[7]

Experimental Section

All experiments were carried out under strictly anhydrous conditions. Solvents were dried by standard procedures. Nmr conditions and instruments were as previously reported.[8] Internal $Si(CH_3)_4$, internal CCl_3F, and external 85% H_3PO_4 served as references for H^1, F^{19}, and P^{31} nmr spectra, respectively.

Reaction of N,N,N′,N′-Tetramethylspiro[silaimidazolidine] (I) with Phenyltetrafluorophosphorane.—A three-necked flask was equipped with a thermometer, reaching to its bottom, a reflux condenser, topped by a drying tube, and a dropping funnel with a side arm. The system was evacuated and filled with dry nitrogen. Over a period of 1 hr, 12.0 g (0.06 mol) of N,N,N′,-N′-tetramethylspiro[silaimidazolidine][5] was added dropwise with stirring to 46 g (0.25 mol) of phenyltetrafluorophosphorane.[9] A vigorous reaction with formation of gas occurred and was controlled by external cooling with ice. The gas coming off the reaction mixture was not held back by a −78° trap, as expected for SiF_4.

The liquid reaction mixture was allowed to stand overnight. By distillation *in vacuo*, 8.0 g (0.044 mol) of unreacted phenyltetrafluorophosphorane (identified by its refractive index) was recovered. The semisolid residue thus left was twice sublimed *in vacuo*. A large amount of a dark brown, involatile oil was left as a residue after the first sublimation. The product was obtained in the form of beautiful white crystals [water-cooled probe; 115° (0.2 mm) oil bath temperature]. Owing to its deliquescent character, the product was handled in a drybox only; no ir spectra were recorded. The yield of IV ($R = C_6H_5$) was 29.0 g (58%, based on I). *Anal.* Calcd for $C_{16}H_{20}F_6N_2P_2$: C, 46.1; H, 4.8; F, 27.4; N, 6.8; P, 14.9. Found: C, 46.4; H, 5.4; F, 26.8; N, 6.7; P, 14.8.

Nmr Spectra.—H^1 (in CH_3CN-d_3): aromatic area of intensity 10 (corresponding to two C_6H_5 groups); a complex multiplet, intensity 4, is due to the two CH_2 groups of the five-membered ring; a doublet ($J_{H-P} = 11.5$ cps) of doublets ($J_{H-F} = 3.7$ cps) is due to the protons of the two CH_3–N groups, split by P^{31} and F^{19}. The spectrum is fully consistent with the structure proposed for IV ($R = C_6H_5$). F^{19} (in CH_3CN): a doublet ($J_{P-F} = 1136$ cps, δ_F +78.7 ppm) is due to the fluorophosphonium cation. The identity of the $C_6H_5PF_5^-$ anion is established from the parameters:[10] $J_{P-F}(eq)$[11] = 820 cps; $J_{F-F}(eq\text{-}ax) = 37$ cps; $\delta_F(eq)$ +57.4 ppm; $J_{P-F}(ax) = 691$ cps; $\delta_F(ax)$ +61.0 ppm; $\delta_F(ax) - \delta_F(eq) = 3.6$ ppm. P^{31} (in CH_3CN):

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[1] Part XVIII: G. S. Reddy and R. Schmutzler, *Inorg. Chem.*, **6**, 823 (1967).

[2] Department of Chemistry, University of Technology, Loughborough, Leicestershire, England.

[3] (a) G. C. Demitras, R. A. Kent, and A. G. MacDiarmid, *Chem. Ind.* (London), 1712 (1964); (b) G. C. Demitras and A. G. MacDiarmid, *Inorg. Chem.*, **6**, 1903 (1967). I am indebted to Dr. Demitras for a copy of this paper in advance of publication and for valuable discussions.

[4] (a) R. Schmutzler, *Angew. Chem.*, **76**, 893 (1964); (b) R. Schmutzler, *Z. Naturforsch.*, **19b**, 1101 (1964); (c) R. Schmutzler, *Chem. Commun.*, 19 (1965); (d) R. Schmutzler, U. S. Patent 3,287,406 (to E. I. du Pont de Nemours and Co., Inc.) (Nov 22, 1966); (e) R. Schmutzler, U. S. Patent 3,300,503 (to E. I. du Pont de Nemours and Co., Inc.) (Jan 24, 1967).

[5] C. H. Yoder and J. J. Zuckerman, *Inorg. Chem.*, **3**, 1329 (1964).

[6] F. A. Henglein and K. Lienhard, *Makromol. Chem.*, **32**, 218 (1959).

[7] For a recent review of chemical and stereochemical aspects of fluorophosphoranes, see R. Schmutzler, "Halogen Chemistry," Vol. 2, V. Gutmann, Ed., Academic Press Inc., New York, N. Y., 1967, pp 31–113.

[8] G. S. Reddy and R. Schmutzler, *Z. Naturforsch.*, **20b**, 104 (1965).

[9] (a) R. Schmutzler, *Inorg. Chem.*, **3**, 410 (1964); (b) R. Schmutzler, *Inorg. Syn.*, **9**, 63 (1967).

[10] For nmr data of authentic $C_6H_5PF_5^-$, see G. S. Reddy and R. Schmutzler, *Inorg. Chem.*, **5**, 164 (1966).

[11] Eq and ax refer to equatorial and axial positions, respectively, in the octahedral RPF_5^- anion.

1–1 doublet, J_{P-F} = 1145 cps; δ_P −56.1 ppm (due to the fluorophosphonium cation); doublet of partially overlapping quintets, $J_{P-F}(ax)$ = 691 cps; $J_{P-F}(eq)$ = 818 cps; δ_P +138 ppm ($C_6H_5PF_5^-$).

Reaction of N,N,N′,N′-Tetramethylspiro[silaimidazolidine] (I) with Ethyltetrafluorophosphorane.—As in the preceding experiment, 10.0 g (0.05 mol) of I[5] was added dropwise with stirring to 28.6 g (0.21 mol) of ethyltetrafluorophosphorane[9a] over a 1-hr period.

The temperature of the exothermic reaction was kept below 40° by external cooling with ice. Subsequently, the reaction mixture was heated with stirring at 100° for 2 hr, and it solidified when cooled to room temperature. The dark brown product was twice sublimed *in vacuo* to give white crystals [water-cooled probe; 80° (0.2 mm) oil bath temperature]. The extremely deliquescent product was handled in a drybox only. The yield was 20.0 g (63%, based on I) of IV (R = C_2H_5). *Anal.* Calcd for $C_8H_{20}F_6N_2P_2$: C, 30.0; H, 6.3; F, 35.6; N, 8.8; P, 19.3. Found: C, 29.4; H, 6.3; F, 36.1; N, 8.7; P, 18.9.

Nmr Spectra.—Because of its expected complexity (overlap of cationic and anionic ethyl resonances) the H^1 spectrum of IV (R = C_2H_5) was not recorded. F^{19} (in CH_3CN): a high-field doublet (J_{P-F} = 1168 cps; δ_F +67.1 ppm) is due to the fluorophosphonium cation. The following parameters were observed for the $C_2H_5PF_5^-$ anion: $J_{P-F}(ax)$ = 680 cps; $J_{P-F}(eq)$ = 850 cps; $J_{F-F}(eq-ax)$ = 32 cps; $\delta_F(ax)$ +57.4 ppm; $\delta_F(eq)$ +56.0 ppm; $\delta_F(ax) - \delta_F(eq)$ = 1.4 ppm. P^{31} (in CH_3CN): a low-field doublet (broad) (J_{P-F} = 1173 cps; δ_P −76.7 ppm) is observed for the fluorophosphonium cation. For $C_2H_5PF_5^-$ the expected doublet ($J_{P-F}(eq)$ = ~860 cps) of partially overlapping quintets ($J_{P-F}(ax)$ = ~650 cps) is observed; δ_P +126.5 ppm.

Reaction of 1,2,2,3-Tetramethyl-1,3-diaza-2-silacyclopentane (II) with Phenyltetrafluorophosphorane.—Under the same experimental conditions as in the preceding experiments, 36.8 g (0.2 mol; 26.6 ml) of phenyltetrafluorophosphorane[9] was added dropwise with stirring over 1 hr to 28.9 g of II.[6] This compound was prepared by the transamination of bis[diethylamino]dimethylsilane, $[(C_2H_5)_2N]_2Si(CH_3)_2$, with N,N′-dimethylethylenediamine; bp 135°, $n^{23.5}D$ 1.4435 (lit.[6] bp 133°, $n^{20}D$ 1.4430). A vigorous reaction took place and a dark brown oil started to separate from the reaction mixture. After the addition was completed, the temperature was raised to 120° for 1 hr. Dimethyldifluorosilane (17.2 g; 90%) was collected in a −78° trap and was identified by ir spectroscopy.[12]

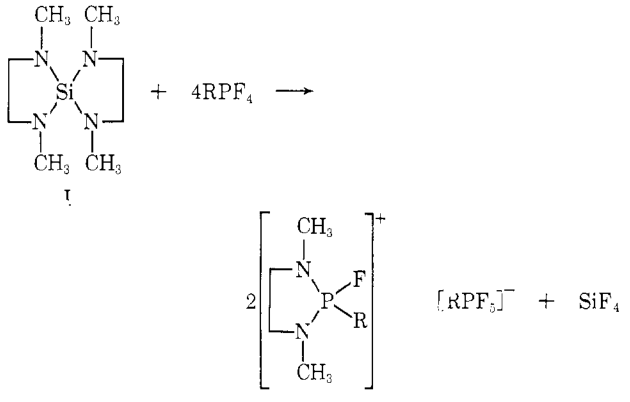
After products volatile at 30° (0.5 mm) had been pumped off, a sticky, semisolid product was left which was transferred to a sublimation apparatus. No sublimation was observed after two heating periods of 15 hr (120°) and 4 hr (180°), both at 0.3 mm. It was concluded that the product was not sublimable and it was extracted for 15 hr in a Soxhlet apparatus with 500 ml of acetonitrile. A 400-ml quantity of acetonitrile was then removed by distillation; the remaining liquid (*ca.* 100 ml) was cooled for 2 days at −10°, after 50 ml of petroleum ether (bp 60–80°) had been added. Hard, white crystals were obtained (V) which were once more recrystallized from acetonitrile–petroleum ether. The product is completely stable in the atmosphere. The yield of V was 24.0 g; mp 178–179°. *Anal.* Calcd for $C_{36}H_{50}F_{10}N_6P_4$: C, 49.1; H, 5.7; F, 21.6; N, 9.6; P, 14.1. Found: C, 49.2; H, 5.6; F, 21.8; N, 9.6; P, 14.1.

Ir Spectrum (KBr Pellet). Values in cm^{-1}: ~3060, 2950, 2880 (m); 2836 (m; CH_3–N); 1597 (m); 1480, 1448 (vs); 1360, 1350 (s); 1320 (m); 1268, 1253 (m); 1210 (s); 1157 (s); 1128 (vs); 1097 (m); 1041 (s); 1006 (vs); 950 (s); 782 (vs); 748 (s); 710, 705 (s); 685 (m); 645 (m); 613 (vs); 554, 548 (s); 530, 518, 499 (m).

Nmr Spectra.—H^1 (in CH_3CN-d_3): an aromatic area, spread out between −7 and −8 ppm, is due to the protons of the four C_6H_5 groups, two in the cation and two in the anion; relative intensity 20. A multiplet of relative intensity 12, centered at −3.23 ppm, is due to the protons of the three ethylene bridges. Finally, there are two doublets of combined relative intensity 18. One of the doublets (J_{H-P} = 11.2 cps; δ_H −2.71 ppm) is due to the two bridging CH_3–N groups, the other (J_{H-P} = 10.8 cps; δ_H −2.63 ppm) is due to the four CH_3 groups attached to the ring nitrogen atoms. F^{19} (in CH_3CN): $C_6H_5PF_5^-$ [10] is clearly the only fluorine-containing species present, the following parameters being observed: $J_{P-F}(eq)$[11] = 822 cps; $J_{P-F}(ax)$ = 693 cps; $\delta_F(eq)$ +57.0 ppm; $\delta_F(ax)$ +60.7 ppm; $\delta_F(ax) - \delta_F(eq)$ = 3.7 ppm; $J_{F-F}(eq-ax)$ = ~35 cps. P^{31} (in CH_3CN): owing to limited solubility, only the low-field part of the spectrum could be recorded with accuracy, but $C_6H_5PF_5^-$ (δ_P +136 ppm) is unambiguously identified by the F^{19} spectrum. A single peak, due to the bis-phosphonium cation of V, is observed at −49.5 ppm.

Results and Discussion

The reaction between the cyclic aminosilanes and two representative fluorophosphoranes proceeded readily under mild evolution of heat with cleavage of all of the Si–N bonds, silicon being eliminated in the form of SiF_4 (from I) or dimethyldifluorosilane, $(CH_3)_2SiF_2$ (from II), respectively. However, the expected fluorophosphoranes of type III were not obtained as such. These compounds apparently function as fluoride ion donors and were invariably isolated in the form of 1:1 adducts with the fluorophosphorane, $C_6H_5PF_4$ or $C_2H_5PF_4$. The structure of these adducts (IV) could be deduced from their H^1, F^{19}, and P^{31} nmr spectra (see Experimental Section).[13] The over-all reaction involving I and the tetrafluorophosphoranes is represented, therefore, by[14]



I

IV, R = C_2H_5, C_6H_5

A product of type III or IV was to be expected in the reaction of II with a tetrafluorophosphorane. Significantly, a different course of reaction was observed here, in accord with the following equation.

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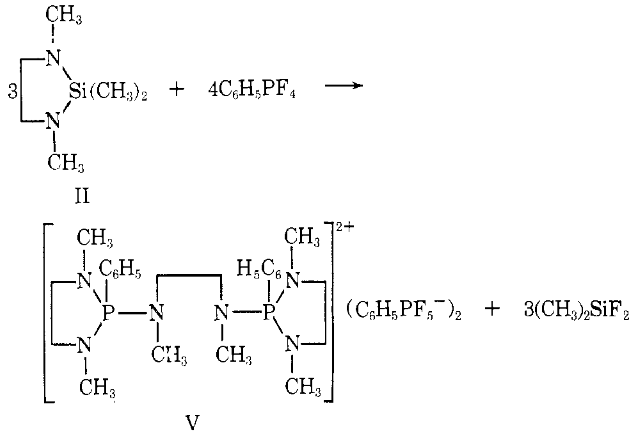
(12) H. Kriegsmann, *Z. Elektrochem.*, **62**, 1033 (1958).

(13) A referee has suggested that a reservation may be indicated, concerning the structure of IV in media less polar than acetonitrile or in the solid state or melt where covalent forms isomeric to IV may exist. It appears that such a possibility can be ruled out for several reasons: while the compounds (IV) are very soluble in acetonitrile, their solubility in less polar solvents is negligible, and no solutions strong enough to permit observation of their nmr spectra could be obtained. Furthermore, a sample of IV (R = C_6H_5) was heated above its melting point (*ca.* 115°) for 15 hr. The F^{19} and P^{31} spectra of the neat, supercooled melt, recorded at room temperature, were completely unchanged to those of the original sample of IV (R = C_6H_5) in acetonitrile. I am indebted to Dr. M. Murray, Department of Chemistry, University of Technology, Loughborough, Leicestershire, England, for this nmr work.

(14) The new 1,3-dimethyl-1,3-diazaphosphacyclopentane ring system in IV and V has been described in the form of some derivatives in several recent publications which appeared after completion of the present work: (a) K. Utvary, V. Gutmann, and Ch. Kemenater, *Inorg. Nucl. Chem. Letters*, **1**, 75 (1965); (b) C. H. Yoder and J. J. Zuckerman, *J. Am. Chem. Soc.*, **88**, 2170 (1966); (c) H. Ulrich, B. Tucker, and A. A. R. Sayigh, *J. Org. Chem.*, **32**, 1360 (1967); (d) O. J. Scherer and J. Wokulat, *Z. Naturforsch.*, **22b**, 474 (1967).



The reaction amounts to the linking up of two 1,3-diaza-2-phosphacyclopentane units by an N,N′-dimethylethylenediamine bridge. It is of interest that V could also be obtained by the reaction of IV (R = C_6H_5) with the twofold molar amount of N,N′-dimethylethylenediamine, as demonstrated by a comparison of the nmr spectra of both products.

Acknowledgment.—Mr. Martin Dipper, E. I. du Pont de Nemours and Co., Inc., Explosives Department, Eastern Laboratory, Gibbstown, N. J., is thanked for his help in obtaining the nmr spectra.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS 02139

The Solubility of Silver Chloride and Silver Bromide in Molten Lithium Nitrate–Potassium Nitrate Eutectic Mixture

BY J. MÉNDEZ,[1a] I. J. GAL,[1b] AND J. W. IRVINE, JR.

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The solubilities of AgCl and AgBr in molten $LiNO_3$–KNO_3 eutectic mixture were measured as a function of temperature and halide ion concentration. The temperature was varied between 150 and 200° and the concentration of halide ion was varied between 1×10^{-3} and 2×10^{-1} *m*. The solubility products of the silver halides and the stability constants of the halide complexes were evaluated. The dependence on temperature of the stability constants follows the generalized quasi-lattice model developed by Blander.

Measurements of the distribution of $AgCl_2^-$ between an $LiNO_3$–KNO_3 molten salt mixture and an organic solution of tetraheptylammonium nitrate in polyphenyl diluent as a function of chloride concentration made possible the evaluation of the stability constants of the silver chloride complexes AgCl and $AgCl_2^-$.[2] In the present work, another independent method, solubility measurements, is used to extend the study to silver bromide complexes and to introduce the temperature as a variable.

Experimental Section

The characteristics and the preparation of the eutectic $LiNO_3$–KNO_3 molten salt mixture were described previously.[2] The solubility of AgCl(s) and AgBr(s) in the molten nitrate mixture containing (Li,K)Cl and (Li,K)Br, respectively, was measured in the temperature range 150–200° using the radioactive tracer method. The 260-day ^{110m}Ag radiotracer in the form of $AgNO_3$ in nitric acid solution with a specific activity of 17.4 mCi/mg of Ag was obtained from the New England Nuclear Corp. The solubility of silver halide was expressed in molality: S = moles of Ag(I)/1000 g of $(Li,K)NO_3$ mixture.

For each run approximately 100 g of a melt 10^{-3} *m* in $AgNO_3$ containing ^{110m}Ag was prepared and aliquots of 9–10 g were poured into glass test tubes and weighed. Known amounts of KCl or KBr and $LiNO_3$ were added to cover a concentration range of halide between 2×10^{-3} and 4×10^{-1} *m* and to keep the mole ratio of K to Li constant at 1.38. The specific radioactivity of the melt in each tube was determined before the addition of the halide salt and expressed as counting rate per gram of $(Li,K)NO_3$ mixture. The tubes were stoppered and kept in an oven at desired temperature (±1°) for 24 hr so the AgX(s) would settle to the bottom of the tubes. The exposure of tubes to light was minimized. Aliquots of approximately 0.2 g of clear melt were taken every day for 4 days with preheated disposable glass pipets into vials, weighed, dissolved in 6 *M* NH_3, and counted with a well-type scintillation counter. These measurements showed that equilibrium was reached in less than 24 hr. The equilibrium concentration of Ag(I) was calculated from the decrease of radioactivity of the melt and the concentration of X^- assuming that the precipitate formed was AgX(s).

Results

The solubilities of AgCl and AgBr in molten $LiNO_3$–KNO_3 eutectic mixture were measured as a function of temperature and halide ion concentration. In all of the experiments the mole ratio of K^+ to Li^+ was kept constant at 1.38, which is the eutectic ratio for $LiNO_3$ and KNO_3. The nitrate and halides containing this proportion of alkali ions will be denoted MNO_3 and MX, respectively.

The concentration of MCl was varied between 4×10^{-3} and 2×10^{-1} *m* and the temperature was varied

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[1] (a) On leave from the Instituto Central de Quimica, Universidad de Concepcion, Concepcion, Chile; (b) on leave from the Boris Kidrich Institute of Nuclear Sciences, Belgrade, Yugoslavia.

[2] I. Gal, J. Méndez, and J. W. Irvine, Jr., *Inorg. Chem.*, **7**, 985 (1968).